Branching and competition of ultrafast photochemical reactions of cyclooctatriene and bicyclooctadiene

Kyriaki Kosma [1], Sergei A. Trushin, Wolfram E. Schmid [2], Werner Fuß *

Max-Planck-Institut für Quantenoptik, 85741 Garching, Germany

ABSTRACT

The main primary photoproducts of cycloocta-1,3,5-triene (COT) are a strained *mono-E* isomer, *Z,Z*-octatetraene (OT, from electrocyclic ring opening) and benzene + ethylene. We investigated the excited-state dynamics of COT by time-resolved mass spectroscopy, probing by near-IR photoionization. Unexpectedly, we found only one reaction channel. We assign it to the pericyclic reactions. Evidence for an early branching between this and the Z–E channel is taken from previous resonance Raman data. This channel confirms previously formulated rules on the excited states involved, the reaction path and driving forces and contributes to their rationalization. Bicyclo[4.2.0]octa-2,4-diene undergoes only two pericyclic reactions: ring opening to OT and cleavage to benzene + ethylene. We investigated it briefly in its equilibrium mixture with COT. The data are consistent with a common path on the excited surfaces. Suggestions are made for structures of conical intersections, and driving forces are considered. All processes were found to be barrierless.

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1. Introduction

The modern description of photochemical pericyclic reactions [1,2] is based on the following concepts: After vertical excitation of a polyene to the so-called spectroscopic state ($1B_2$ in the frequent molecular symmetry C_{2v}) the molecule is first accelerated along Franck–Condon (FC) active coordinates, which mainly involve the lengths and torsion angles of conjugated π bonds. Thereafter the Woodward–Hoffmann (WH) type σ–π interactions can begin, so that the motion continues on the same electronic surface in a (slightly) different direction towards a conical intersection (CI) with a two-electron excited ("dark", $2A_1$ in C_{2v}) state. This state involves the same two orbitals as $1B_2$ (but with both electrons lifted up), which are just those that cross each other in the WH-type orbital correlation diagram. The orbital crossing causes an avoided crossing of the $2A_1$ and $1A_1$ potentials. The resulting $2A_1$ minimum ("pericyclic minimum" [1,2], which may actually be a saddle point) is lower in energy and more shifted in WH direction than the $1B_2$ minimum. Even further down is a conical intersection (CI) with the ground state ($2A_1/1A_1$ CI). It is typically

displaced into a symmetry-breaking direction. The wave packet hence moves from the $1B_2$ surface around the first CI via the $2A_1$ minimum (acting as a collection well) or directly to the funnel ($2A_1/1A_1$ CI), where it branches to the product(s) and the reactant in their ground states.

This view resulted in particular from quantum chemical (e.g. [2,3]) and time-resolved (e.g. [2,4]) investigations of the electrocyclic ring opening of 1,3-cyclohexadiene. (For more literature, see the two reviews [5,6].) A similar scheme with spectroscopic state, dark state and conical intersections is valid for cis–trans isomerizations of polyenes [7,8]. The majority of the pericyclic and cis–trans isomerizations investigated turned out to be barrierless and hence ultrafast (see the recent compilation in [9]).

Ring opening is practically the only photochemical process of cyclohexadiene, not counting the return from the last CI to the reactant (i.e., internal conversion). On the other hand, there are many molecules exhibiting more than one photochemical reaction at a given excitation wavelength. It seems interesting, where on the potentials the branching(s) occur. One possibility is the FC region; previously this was implicitly assumed in many photochemical investigations, where only states were considered instead of potentials and the paths on them. On considering also the slopes of potentials in this region, it was just recently shown that one can in fact understand a wide variety of the observed selections between different allowed (sometimes also forbidden) pericyclic reactions and cis–trans isomerizations and other phenomena such

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* Corresponding author at: Weidachstr. 12, 85748 Garching, Germany.
E-mail addresses: kosma@iesl.forth.gr (K. Kosma), sergei.a.trushin@mpq.mpg.de (S.A. Trushin), w.fuss@mpq.mpg.de (W. Fuß).
[1] New address: Institute of Electronic Structure and Laser (IESL), Foundation for Research and Technology-Hellas (FORTH), 71110 Heraklion, Crete, Greece.
[2] New address: Gertrud-von-le-Fort-Str. 38, 97074 Würzburg, Germany.

as wavelength dependences [9]. However, also other features later on the surfaces such as ridges and conical intersections are natural branching regions, and the local geometrical structures are usually correlated with the course of the reactions. For example, the cis–trans isomerization and H migration in ethylene and derivatives were suggested to originate from a common CI (or intersection region), in which the two reactions are both half finished [10] (see there for more examples and previous suggestions). We suggest both an early and a late branching for a compound (cyclooctatriene) investigated here.

In this work we use femtosecond-time-resolved mass spectroscopy in the gas phase to study cycloocta-1,3,5-triene (COT) and briefly also its thermal isomer bicyclo[4.2.0]octa-2,4-diene (BCOD). Both molecules show several pericyclic reactions, and COT has a strained *mono-E* isomer even as the main product (Scheme 1, where isomerization at the central double bond was assumed, see Section 4.4). Only flash spectroscopy [11] and matrix isolation [12,13] identified the primary products shown in Scheme 1. Because at room temperature the strained product *mono-E*-COT in the ground state forms *Z,Z*-OT in milliseconds and *Z,Z*-OT closes the ring again within seconds to COT [11], preceding works observed only minor side products and secondary photoproducts (such as trans isomers of OT and others, not shown in the Scheme; see, for example, [14] for an early careful investigation and p. 248 of [15] for a summary including primary products). The photochemical primary products of BCOD are benzene + ethylene and octatetraene [12]. On prolonged storage COT equilibrates in a thermally allowed electrocyclic reaction with BCOD [16,17] (after longer time or at higher temperatures also with cycloocta-1,3,6-triene via sigmatropic 1,5-migration of H [14,17]. All these isomers can also be formed already in the preparation by reduction of cyclooctatetraene [18].). COT can be isolated via its AgNO₃ complex, from where it can again be displaced by concentrated ammonia [16]. We mainly investigated COT prepared in this way, but did some measurements also with the commercial COT/BCOD mixture, so that some conclusions on BCOD are also possible.

The experimental technique is described in our cyclohexadiene work [19], for instance. Briefly, the third harmonic (270 nm) of a Ti-sapphire laser excites the molecules in the gas phase and the fundamental (810 nm) probes them with varying time delay by nonresonant photoionization; the parent and fragment ions are detected depending on this delay. The ionic fragmentation strongly increases, the more energy is released on the path of the wave packet (in the form of kinetic energy) and the more it is displaced; this is because the ionization is vertical, thus conserving the kinetic energy and geometric structure. This rule is not only an assignment help but also provides the chance to extract many time constants, if many fragment ions are recorded. This possibility is important, if one wants to record several processes (photochemical reactions), each of which consisting of more than one step.

Previously we were frequently able to record several branched processes, for example in cyclohepta- and cycloocta-1,3-diene [20], which both undergo Z–E-isomerization and an electrocyclic reaction (ring closure to cyclobutene derivatives). However, in the present work we found less time constants for COT than expected. Perhaps some parallel processes have characteristic times too similar to be distinguished, or alternatively the ionization probability from one of the paths is too small (see Section 4).

A previous attempt at time-resolved mass spectroscopy of COT was unfortunately done with the unseparated mixture [21]. The kinetic analysis was also oversimplified, so that only a limited comparison with the present work is possible. Except COT → OT, the correct reactions were also not recognized. However, valuable complementary information is available from the resonance Raman work of the Mathies group [22–26]; in particular the intensity analysis [22] provided the direction of initial motion, even if
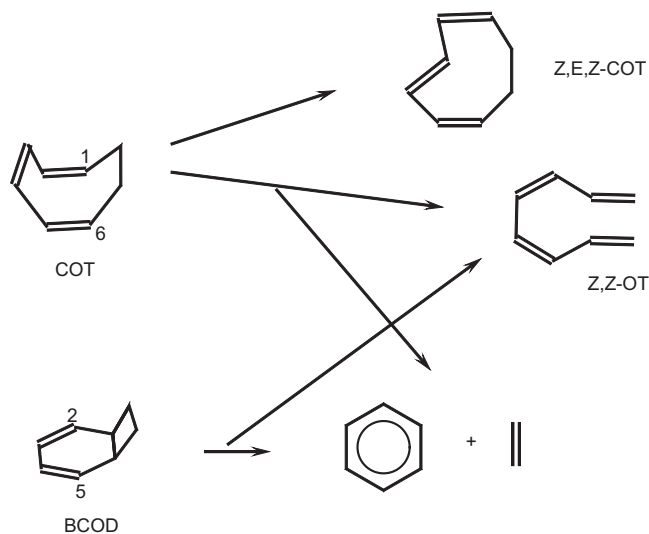
Scheme 1. Primary photoreactions of cyclooctatriene (COT) and bicyclooctadiene (BCOD) according to [11,12]. It is here assumed (see Section 4.4) that it is the central double bond, which rotates to produce the strained isomer. The arrows also hint to the suggested early and late branchings.

the authors only considered COT → OT as reaction. As revealed by the present work, the time resolution (several ps) in this Raman work [26] was, however, not sufficient for the dynamics of these processes. A time-resolved electron diffraction study with its resolution of only 4 ps also did not show the evolution on the potentials but only one of the (primary) products, *Z,Z*-OT and its ground-state rotamerization [27].

For labeling the spectroscopic, the dark and the ground state, we use the symmetry types of C_{2v} ($1B_2$, $2A_1$ and $1A_1$) as in [22–26], who point to the approximate local symmetry of the π system. Actually COT is a twisted boat (with two enantiomeric potential minima) [28,29] and has hence no symmetry (C_1), whereas BCOD has one symmetry plane (C_s).

2. Experimental

The COT/BCOD mixture was purchased from Organometallics (East Hampstead, USA). According to gas-chromatographic mass-spectroscopic analysis, it contained about 20% BCOD besides the COT. The monocyclic compound was isolated from the mixture according to the procedure of [16]: by complexing it with AgNO₃ (1.6 mol per mol of isomers) dissolved in water (30% solution). The precipitate was twice recrystallized from ethanol. From a small sample, COT was displaced by concentrated aqueous ammonia, as in [16]; thereafter, no organic impurity was detectable gas-chromatographically. The main part of the COT was, however, recovered in a simpler way: by decomposing the complex in vacuum at 60–80 °C (1 h), collecting the volatiles in a cold trap. The condensate also showed no BCOD (<0.1%), though it contained traces of water and ethanol. As the latter do not absorb the pump radiation in the near UV and the ions would be easy to distinguish from COT⁺, the sample was used in the experiment without drying.

COT and the unseparated COT/BCOD mixture were investigated at 20 °C in the gas phase. They were introduced through a precision needle valve to the ionization region of a time-of-flight mass spectrometer at a pressure of ≈10⁻⁷–10⁻⁶ mbar, where they were first excited by a weak pump pulse at 270 nm (duration ≈28 fs, intensity ≈10⁹ W cm⁻²) and then ionized with the delayed probe laser at 810 nm (≈17 fs, ≈10¹³ W cm⁻²). (The pump wavelength is within the first strong UV band of both compounds [16].) The probe radiation was generated by shortening of pulses from a